# *Some Experiments on Thermal Diffusion.*

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*With a Note on the Experiments by* Prof. S. Chapman, F.R.S.

(Communicated by Prof. S. W. J. Smith, F.R.S. Received March 16, 1921.)

## *Introduction.*

It has been shown theoretically by Dr. S. Chapman* that a temperature gradient applied to a uniform mixture of two gases will tend to produce non-uniformity of composition, the heavier and larger molecules diffusing towards the cooler side, and the smaller and lighter molecules diffusing towards the hotter side. This phenomenon was termed "thermal diffusion." The difference in composition due to thermal diffusion increases until it is balanced by the opposite effects of ordinary diffusion, when a steady state will be reached. The effect will be greatest when the gases are mixed in nearly equal proportions by volume, and will be greater the more unequal are the masses and diameters of the gas molecules. It was also shown that the extent of the effect would vary with the character of the gas molecules, being at a maximum when the molecules behave like rigid elastic spheres. In the case where molecules behave like fifth power centres of force the effect would disappear entirely.

Experiments made by Chapman and Dootson† established the existence of the phenomenon. The results were chiefly qualitative, the nature and order of magnitude being in agreement with the theory. In no case were the differences equal to the theoretical values obtained on the assumption that gas molecules behave like rigid elastic spheres. Although the results are not claimed to be exact, the general effect could be regarded as rather less than a half of this calculated effect. The character of the gas molecule required to give this result would, however, be in agreement with that obtained for the actual gas molecules from the investigation of the variation of viscosity with temperature.

The method used by the writer in carrying out the following experiments depends on the use of the katharometer‡ for accurate gas analysis. The apparatus was devised shortly after the appearance of Dr. S. Chapman's paper in 1916, by Dr. G. A. Shakespear, who, when opportunity occurred in December, 1918, tested Chapman's predictions. The gases used were coal gas and also mixtures of carbon dioxide and hydrogen, and a wide range of temperature differences was tried. The results being satisfactory Dr. Shakespear suggested to the present writer that a more detailed investigation would be of interest. I am indebted to Dr. Shakespear for the use of the apparatus and for valuable advice and assistance in carrying out the work. The mixtures of gases used throughout these experiments were of hydrogen and carbon dioxide in definite proportions. These lend themselves particularly well to detection by the katharometer of any changes in composition due to thermal diffusion: the action of the instrument depending on the differences of thermal conductivity of various gases.

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* 'Phil. Trans.,' A (1916).

† 'Philosophical Magazine,' March, 1917—"A Note on Thermal Diffusion."

‡ *Cf.* G. A. Shakespear, "Note on the Katharometer," 'Roy. Soc. Proc.,' vol. 97, p. 273 (1920).

### *Method of Experiment.*

A katharometer ($K_1$) was first calibrated by using nine known mixtures of the two gases made up in small quantities for this purpose, the mixtures in turn being exposed to $r_2$, and the deflection on $G_1$ noted. The electrical arrangement, which is the normal one, is shown diagrammatically in fig. 1. A graph showing composition and galvanometer deflection was plotted (fig. 2), and by reference to this the composition of any other mixture of the gases can be determined by means of the katharometer.

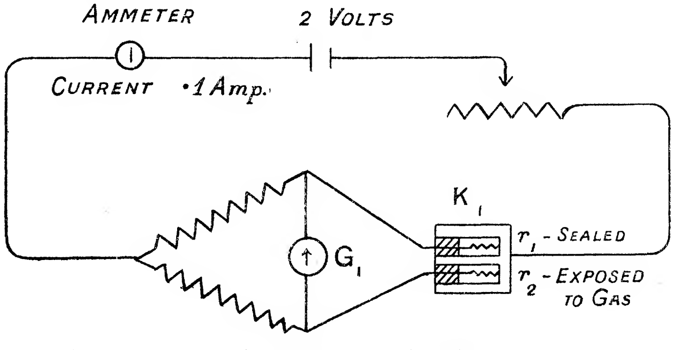

Fig. 1.—Electrical arrangement of katharometer $K_1$.

The mixtures for the actual experiments were required in considerable quantity, and they were made up under pressure in a 4 cubic feet cylinder. The composition of the contents of the cylinder was determined accurately in the way shown above.

A known mixture was passed from the cylinder through the apparatus shown in fig. 3. This apparatus, which can be termed the separator, consists essentially of a cylindrical glass vessel, down the middle of which runs a spiral of platinum wire. The spiral can be heated by passing a current through it. The gas mixture enters at A, passes upwards through the chamber B, and goes out either through C or D. Tube C takes the gas from the cooler and outer part of the vessel, and tube D which surrounds the top of the hot spiral takes the gas from the middle and hotter part. During an experiment the gas was allowed to flow steadily through the apparatus. After passing out through C and D, the gas was passed through copper coils in order to equalise the temperatures of the two streams.

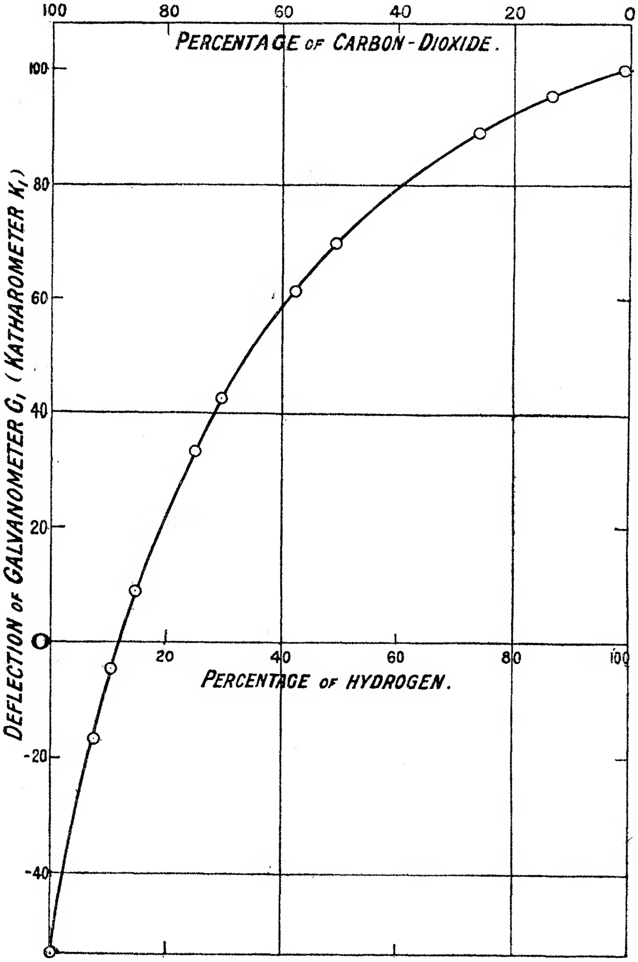

Fig. 2.

In order to detect and measure any difference in composition between the gases issuing from the two branches of the separator, use was made of a double flow or differential katharometer ($K_2$) through which the two streams of gas were passed.

This instrument is similar to the ordinary form except that in this case, instead of one cell being sealed and the other exposed to the gas, each cell communicates by small apertures with another cell exposed to the gas issuing from one branch of the separator. A difference in composition between the gases coming from the hot and cold sides will be detected by their difference in thermal conductivity. Fig. 4 is a diagrammatic representation of $K_2$, showing the two cells of the katharometer exposed to the gases. The electrical arrangement is the same as for $K_1$ (shown in fig. 1). Any difference in composition between the gases on the two sides of the katharometer upsets the balance of the bridge and causes a deflection on the galvanometer ($G_2$). In this case a reflecting galvanometer was used, greater sensitiveness being required. For a mixture of initial composition 50 per cent. hydrogen and 50 per cent. carbon dioxide, a percentage difference between the compositions of the gases on the two sides of less than 0·006 could be measured. For mixtures containing less hydrogen the instrument is more sensitive, and *vice versâ*. In the case of a mixture of 2 per cent. hydrogen and 98 per cent. carbon dioxide a difference of 0·001 per cent. could be measured, and with a

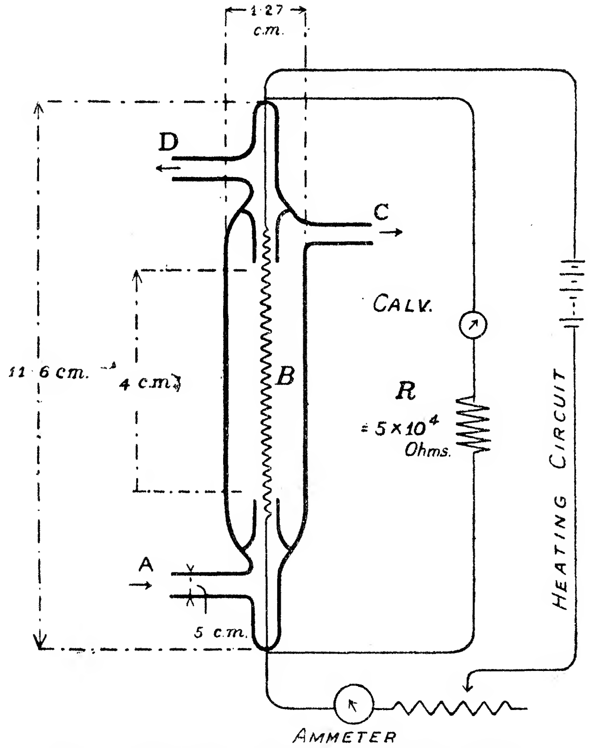

Fig. 3.—Separator with Electrical Connections.

mixture of 87 per cent. hydrogen and 13 per cent. carbon dioxide a difference of 0·01 per cent.

A calibration of $K_2$ was necessary to get the values of the differences in composition between the gases on the two sides, from the deflections of the galvanometer $G_2$. To effect this the apparatus shown in fig. 5 was used. For each mixture used in the experiments, a known small difference of composition was made in the following way. A gas mixture of known composition flows in at A, and divides into the two arms B and C. At E, in the arm C, a small quantity of hydrogen is introduced. This mixes in the chamber D, and the composition of the new mixture is determined by the katharometer $K_1$ (from the deflection of $G_1$—not shown in diagram). The mixtures in the two arms B and C now pass through the two sides of the differential katharometer $K_2$, the difference in composition causing a deflection of $G_2$ (not shown). Knowing the actual difference of composition in this case, we are able to get the meaning of a deflection of $G_2$ in terms of the difference in composition between the gases on the two sides of the katharometer.

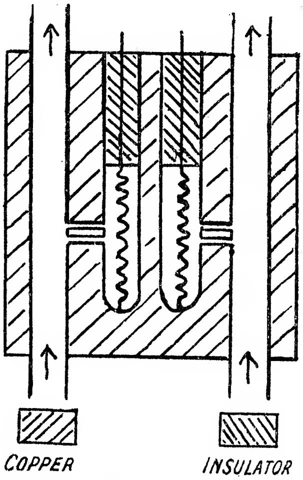

Fig. 4.—Differential katharometer, showing both cells exposed to gases.

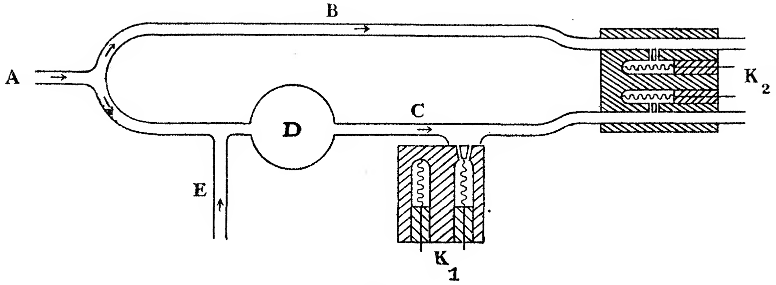

Fig. 5.

The temperature of the platinum helix in the separator was varied by altering the current passing through it (fig. 3); the current being increased by regular amounts until the helix became red hot at about 600° C. The temperature gradient in the separator was from the temperature of the hot spiral down to that of the surrounding glass walls of the apparatus, *i.e.*, roughly, the room temperature (about 16° C.). No special cooling device was used for keeping cool the outer walls of the apparatus, so that the real gradient of temperature in the separator was rather less than the calculated gradient. Thus it was found that, when the temperature of the heating spiral was increased, the amount of separation rose to a maximum, and then fell slightly, owing to the rise in temperature of the outer walls of the apparatus. For calculating the temperature of the spiral, it was necessary to know the potential difference between its ends, its resistance at a known temperature, and the temperature coefficient of resistance of the material of the wire, in addition to the current flowing through it. The potential difference was obtained by joining the ends of the spiral in series with a galvanometer and a resistance of $5 \times 10^4$ ohms (fig. 3), the galvanometer thus being used as a voltmeter. The calibration of this galvanometer and resistance as a voltmeter was made by a potentiometer method, using a Clark cell as a standard. The temperature coefficient of resistance for the platinum helix was found by measuring its resistance by a P.O. box at three known temperatures. A graph of temperature and resistance of the spiral was plotted by using a number of calculated values up to a temperature of 700° C., and, by reference to this, the temperature corresponding to any particular resistance could be obtained.

The method differed essentially from those of Chapman and Dootson, in that the thermal separation was continuous: a steady flow of the mixture being maintained in the separator, and the partially separated gases passing out on the hot and cold sides, the difference in composition being at once shown by the katharometer. This form of apparatus is well adapted for finding the effect of alteration of temperature gradient on the amount of thermal separation. The gases were allowed to pass through a water bubbler before finally escaping into the air. This served as a means of indicating the rate of flow through the apparatus, enabling a uniformly slow and steady flow to be maintained. The gas passed through each side of the bubbler at the same rate, which meant that approximately equal amounts of gas were being taken from the hot and cold regions of the separator. A steady state of separation (as indicated by galvanometer $G_2$) was reached after a mixture had been passing through the separator for about three minutes. The amount of separation obtained was not affected by the rate of flow through the separator, provided that the rate of flow was not made too great.

### *Results of Experiments.*

Experiments were made on the following twelve different mixtures of carbon dioxide and hydrogen.

Table I.

| Mixture No. | $H_2$. | $CO_2$. | Room temperature. |
|---|---|---|---|
| | per cent. | per cent. | ° C. |
| 1 | 2·0 | 98·0 | 12 |
| 2 | 7·7 | 92·3 | 13 |
| 3 | 10·7 | 89·3 | 13 |
| 4 | 19·7 | 80·3 | 17 |
| 5 | 24·2 | 75·8 | 13 |
| 6 | 38·0 | 62·0 | 13 |
| 7 | 41·5 | 58·5 | 17 |
| 8 | 50·0 | 50·0 | 16 |
| 9 | 55·5 | 44·5 | 16 |
| 10 | 61·0 | 39·0 | 16 |
| 11 | 72·5 | 27·5 | 16 |
| 12 | 86·5 | 13·5 | 17 |

In each case readings were taken with the platinum spiral of the separator varying between room temperature and red heat, thus giving temperature differences up to a maximum of about 600° C. The following Table of Results obtained from Mixture No. 10 may be regarded as a typical set:—

Table II.

Mixture No. 10. Composition: 61·0 per cent. $H_2$, 39·0 per cent. $CO_2$.
Room temperature 16·2° C.

| Current in heating spiral. | Voltage between ends of spiral. | Resistance of spiral. | Temperature of spiral. | Percentage separation between gases from hot and cold sides. | Hence final composition. | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Hot side. | | Cold side. | |
| | | | | | H. | $CO_2$. | $H_2$. | $CO_2$. |
| amp. | volts. | ohms. | ° C. | p.c. | p.c. | p.c. | p.c. | p.c. |
| 0·05 | 0·82 | 16·40 | 25 | 0·045 | 61·022 | 38·978 | 60·978 | 39·022 |
| 0·10 | 1·66 | 16·60 | 35 | 0·157 | 61·078 | 38·922 | 60·922 | 39·078 |
| 0·15 | 2·52 | 16·80 | 45 | 0·344 | 61·172 | 38·828 | 60·828 | 39·172 |
| 0·20 | 3·52 | 17·60 | 80 | 0·600 | 61·300 | 38·700 | 60·700 | 39·300 |
| 0·25 | 4·60 | 18·40 | 115 | 0·891 | 61·445 | 38·555 | 60·555 | 39·445 |
| 0·30 | 5·71 | 19·00 | 145 | 1·22 | 61·61 | 38·39 | 60·39 | 39·61 |
| 0·35 | 7·00 | 20·00 | 190 | 1·56 | 61·78 | 38·22 | 60·22 | 39·78 |
| 0·40 | 8·42 | 21·05 | 240 | 1·92 | 61·96 | 38·04 | 60·04 | 39·96 |
| 0·45 | 10·10 | 22·30 | 300 | 2·29 | 62·14 | 37·86 | 59·86 | 40·14 |
| 0·50 | 11·76 | 23·52 | 365 | 2·61 | 62·30 | 37·70 | 59·70 | 40·30 |
| 0·55 | 13·51 | 24·55 | 420 | 2·84 | 62·42 | 37·58 | 59·58 | 40·42 |
| 0·60 | 15·56 | 25·93 | 500 | 3·31 | 62·65 | 37·35 | 59·35 | 40·65 |
| 0·65 | 17·62 | 27·20 | 570 | 3·52 | 62·76 | 37·24 | 59·24 | 40·76 |

The difference in composition due to thermal diffusion between the gases issuing from the hot and cold sides of the separator will, for the rest of this paper, be expressed simply as a percentage separation. In all cases the quantity of gas issuing from the two sides was practically the same, so that the actual composition of these gases can easily be found, if required, as in the last columns of the Table shown above. The effects of thermal diffusion were clearly observed in all the experiments, the excess of hydrogen always being found in the gas coming from the hot side and of carbon dioxide in the gas from the cold side. The results also show the increase of the effect with the increase of the temperature gradient.

To avoid giving large masses of data, the results are briefly summarised in

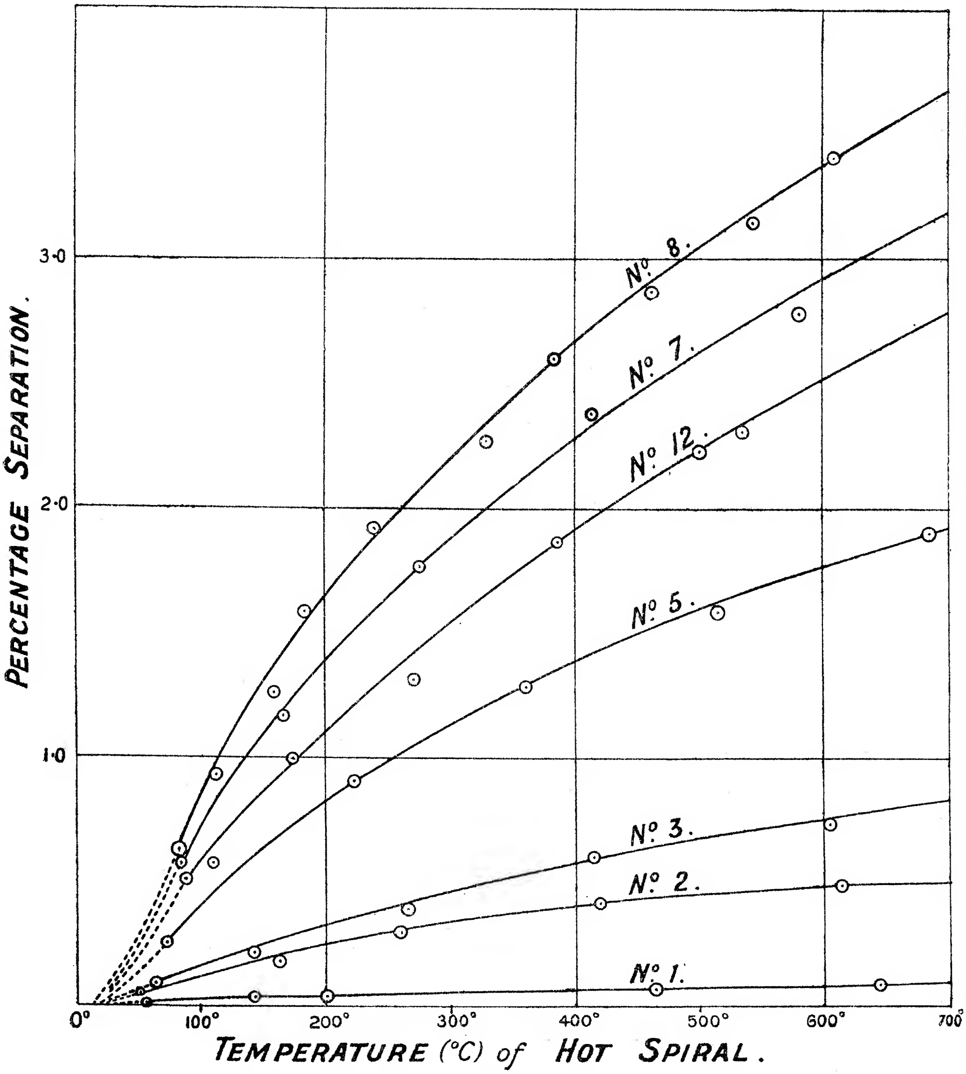

Fig. 6.—Temperature-separation curves for Mixtures 1, 2, 3, 5, 7, 8, 12. (See Table I.)

the form of curves showing the temperature of the hot spiral and the resulting percentage separation. Such curves for Mixtures Nos. 1, 2, 3, 5, 7, 8, and 12 are shown in fig. 6. Each curve represents a complete series of experiments.

By using such a series of graphs the relation between the amount of separation and the composition of the original gas mixture, for any definite temperature gradient, can be investigated. For example, we can pick out the different amounts of separation in each for a temperature difference of, say, 200° C.; and combining these with the corresponding composition of the original gas, construct another diagram. Such diagrams are shown in fig. 7 for temperature differences of 100°, 200°, 400°, and 600° C. It will be observed that these diagrams all have the same general form, the amount of separation increasing from zero to a maximum, and then diminishing to zero, in each case the maximum separation being shown for a mixture containing from 50 to 60 per cent. of hydrogen. This experimental result is in agreement with the theory of Chapman, who showed that the maximum separation should occur in mixtures containing about 50 per cent. of each gas. Although the general form of the curves is apparent the points do not lie as uniformly as those on the temperature-separation curve for a given mixture. This may be expected from the fact that the points are obtained from different sets of experiments, in which the only check on getting an equal flow of gas from the hot and cold sides was by passing it through a water-bubbler.

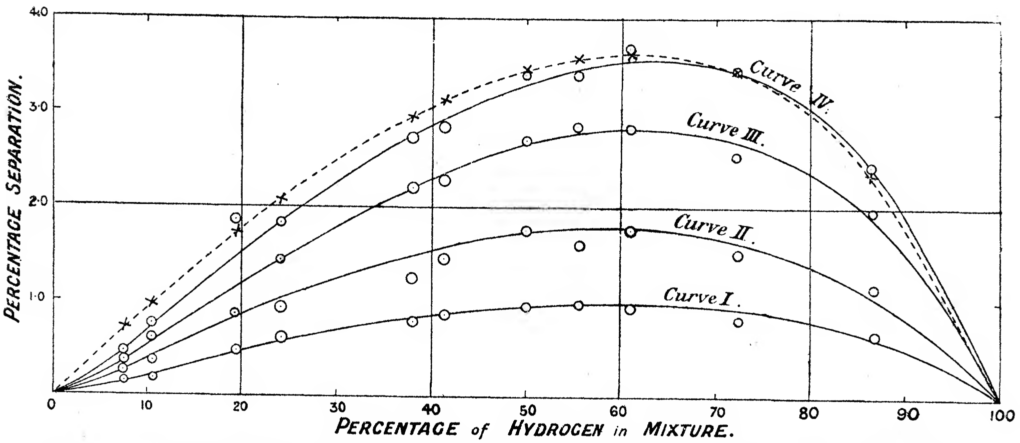

FIG. 7.—Relation between composition and separation with a given temperature difference.

Curve I—100° C. difference; Curve II—200° C. difference; Curve III—400° C. difference; Curve IV—600° C. difference; Dotted Curve—Obtained from values of $Ck_t$ calculated.

## *Analysis and Summary of Results.*

The following relation was deduced theoretically by Chapman. If the absolute temperature is denoted by T, and the proportion by volume of the heavier and lighter gases by $v_1$ and $v_2$ respectively (so that $v_1+v_2 = 1$), then in the steady state the concentration and temperature gradients at a point $(x . y . z)$ are related to one another by three $(x . y . z)$ equations of the form

$$\frac{d}{dx}\left(\frac{v_1}{v_1+v_2}\right) = -\frac{d}{dx}\left(\frac{v_2}{v_1+v_2}\right) = k_t \frac{d}{dx}(\log \mathrm{T}),$$

where $k_t$ is the ratio of the ordinary coefficient of diffusion to the coefficient of thermal diffusion. Consequently it follows that over a distance within which $k_t$ may be regarded as constant, $v_1/v_1+v_2$ varies as log T.

A further series of graphs have been plotted showing percentage separation and $\log_{10} \mathrm{T}_1/\mathrm{T}_2$, where $\mathrm{T}_1$ is the absolute temperature of the spiral and $\mathrm{T}_2$ is the room temperature. These graphs for Mixtures Nos. 2, 4, 6, 10, and 12 are shown in fig. 8. The general form of these graphs approximates closely to a straight line when the temperature differences exceed about 100° C. The slight irregularity near the origin may be due to the form of the heating spiral. The nature of these graphs may be regarded as constituting a striking experimental verification of the theory.

The greatest percentage separation obtained in the experiments was 3·52 for mixture No. 10 (61 per cent. $H_2$ and 39 per cent. $CO_2$), with a temperature difference of 557° C. Chapman and Dootson obtained a greatest percentage separation of 3·6, using the same gases (43·1 per cent. H and 56·9 per cent. $CO_2$), with a temperature difference of 220° C. The smaller amount of separation is to be expected from the form of apparatus used, in which the area of the hot spiral is small compared with that of the outer glass walls of the separator. The simpler form of separating device employed by Chapman and Dootson facilitates calculations involving temperature gradient and the absolute amount of separation obtained. The shape of the heating spiral, and the fact that there is a continuous current of gas through the apparatus, make it impossible to calculate the configuration of the gas at the higher temperature. In this sense the results are comparative only: we cannot obtain a value for $\mathrm{K}_t$ and compare it with values obtained theoretically. The results of the experiments, therefore, do not furnish any information as to the nature of the molecular model which would most nearly represent the actual gas molecules. They do, however—

(*a*) Provide a verification by a new method of part of the results obtained by Chapman and Dootson.

(*b*) Show that the maximum separation due to thermal diffusion is obtainable in a mixture containing 50–60 per cent. of the lighter gas.

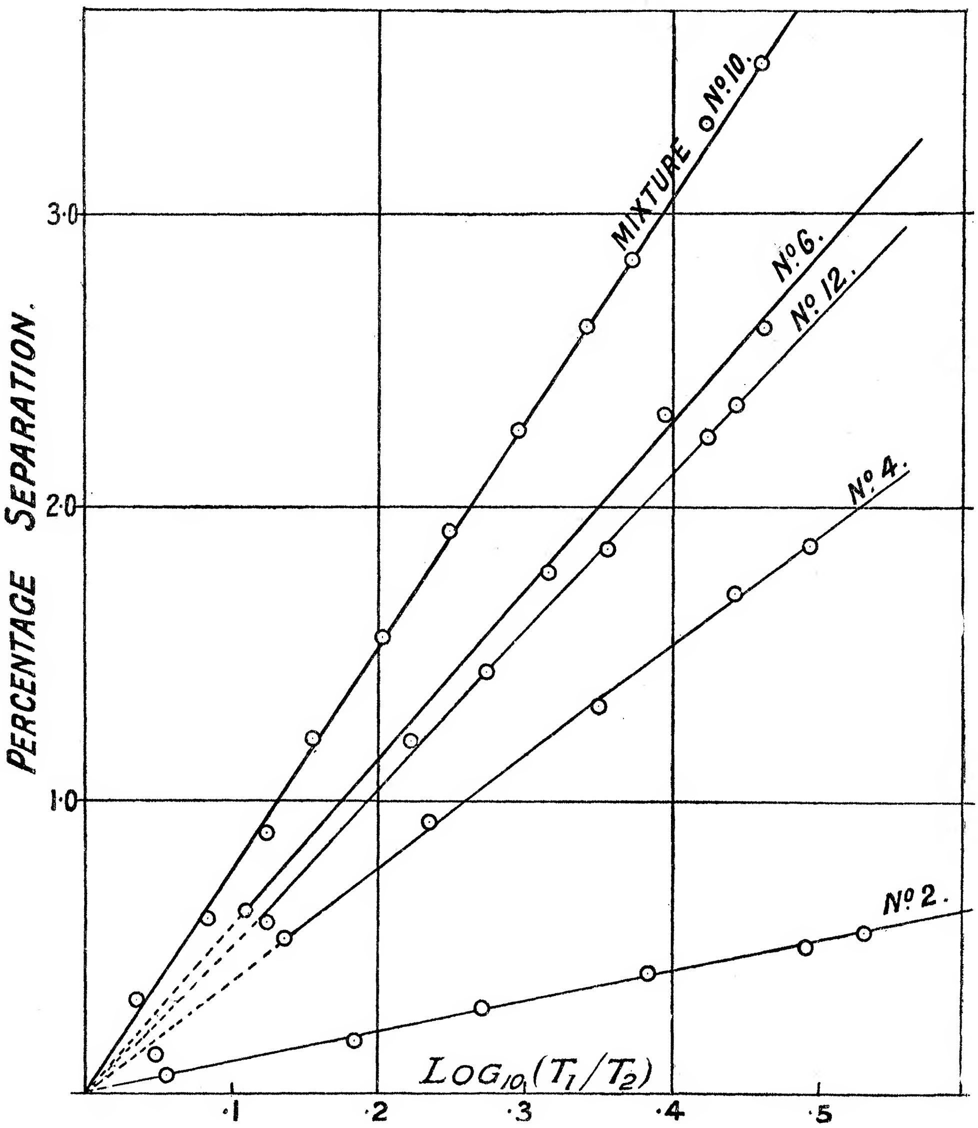

Fig. 8.—Relation between percentage separation and $\log_{10} T_1/T_2$ for Mixtures 2, 4, 6, 10 and 12.

(*c*) Show that the amount of separation varies as $\log T_1/T_2$, where $T_1$ and $T_2$ are the absolute temperatures forming the temperature gradient.

## *Note on Mr. T. L. Ibbs' Experiments.*

By Prof. S. CHAPMAN, F.R.S.

Mr. Ibbs' interesting and accurate experiments may advantageously be compared, in rather more detail than he has done, with the theoretically predicted influence of the ratio of the two gases in a mixture upon the coefficient of thermal diffusion $k_t$. It is sufficient to consider the simple formula giving the first approximation to $k_t$ (correct to within a few per cent.) for rigid elastic spherical molecules. The value of $k_t$ for actual gas molecules is probably only about half that calculated for this molecular model, but the variation with the ratio of mixture is likely to be nearly the same in the two cases.

The formula in question, with numerical values inserted for the $H_2$–$CO_2$ mixture, is*

$$k_t = \frac{0{\cdot}331\lambda_1 + 0{\cdot}0542\lambda_2}{47{\cdot}2 + 86{\cdot}5\lambda_{12} + 5{\cdot}58\lambda_{21}};$$

$\lambda_1$, $\lambda_2$ are the percentages, by volume, of carbon dioxide and hydrogen respectively, while $\lambda_{12} \equiv \lambda_1/\lambda_2$, $\lambda_{21} \equiv \lambda_2/\lambda_1$. The following values are calculated for the twelve mixtures used by Mr. Ibbs:—

| Mixture. | 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|---|
| $k_t$ .................. | 0·008 | 0·029 | 0·039 | 0·069 | 0·082 | 0·118 |
| $Ck_t$ .............. | 0·2 | 0·72 | 0·97 | 1·72 | 2·05 | 2·95 |

| Mixture. | 7. | 8. | 9. | 10. | 11. | 12. |
|---|---|---|---|---|---|---|
| $k_t$ .................. | 0·125 | 0·138 | 0·144 | 0·146 | 0·138 | 0·095 |
| $Ck_t$ .............. | 3·12 | 3·45 | 3·60 | 3·65 | 3·45 | 2·37 |

The last row is added to facilitate comparison with the uppermost curve in fig. 7, with which the curve for $k_t$ is, as it should be, very closely similar.

As regards the absolute amount of separation found by Mr. Ibbs, it is sufficient to consider mixture No. 10, for which fig. 8 shows a separation of 3·85 per cent. when $\log_{10} T_1/T_2 = 0{\cdot}5$. The theoretical amount for rigid spherical molecules is $0{\cdot}146 . \log_e 10 . 0{\cdot}5$, or 16·8 per cent.; the observed value is much less, partly because of the molecular model above used, which makes $k_t$ about twice too great; and, secondly, because $T_1/T_2$ measures the ratio of the extreme temperatures in the separator, and not the ratio of the mean temperatures of the two halves of the gas.

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* 'Phil. Mag.,' vol. 33, p. 522 (1917).

A point of special interest in Mr. Ibbs' paper is the shortness of the time, about three minutes, required for thermal diffusion to take effect.

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# *The Dynamics of Revolving Fluid on a Rotating Earth.*

By Capt. D. Brunt, M.A., B.Sc.

(Communicated by Sir Napier Shaw, F.R.S. Received April 6, 1921.)

In a paper on the dynamics of revolving fluids, the late Lord Rayleigh* considered the special case of fluid revolving about a fixed vertical axis, neglecting the rotation of the earth. The object of the present paper is to investigate the modifications of Rayleigh's results which are brought about by the rotation of the earth, and by translation in a vertical plane of the axis of symmetry. Air is treated as an incompressible non-viscous fluid.

Let the motion be referred to rectangular axes, $x$, $y$, $z$, rotating with the earth, the axis of $z$ being vertical and the axes of $x$ and $y$ in the horizontal plane. At a point $x$, $y$, $z$, the components of velocity are $u$, $v$, $w$, the pressure is $p$, and density $\rho$. If gravity is the only impressed force, the equations of motion are

$$\mathrm{D}u/\mathrm{D}t = -1/\rho \, dp/dx + lv, \tag{1}$$

$$\mathrm{D}v/\mathrm{D}t = -1/\rho \, dp/dy - lu, \tag{2}$$

$$\mathrm{D}w/\mathrm{D}t = -1/\rho \, dp/dz + g, \tag{3}$$

where $$\mathrm{D}/\mathrm{D}t = d/dt + u\, d/dx + v\, d/dy + w\, d/dz$$

and the equation of continuity is

$$du/dx + dv/dy + dw/dz = 0, \tag{4}$$

where $l = 2\omega \sin\phi$, $\omega$ being the angular velocity of rotation of the earth, and $\phi$ the latitude. The terms $lv$, $-lu$, in the first two equations represent components of the deviating force due to the earth's rotation, and the inclusion of these terms takes complete account of the rotation of the earth.

If values of $u$, $v$, $w$, $p$, be found to satisfy equations (1) to (4), then if U be a constant, $u+\mathrm{U}$, $v$, $w$, $p-\rho l\mathrm{U}y$ will also satisfy these equations. In other words, to any system of velocities which satisfies the equations there may

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* 'Roy. Soc. Proc.,' A, vol. 93, p. 148 (1916).